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EXTERNAL FIELD IN LANDAU THEORY OF THE WEAKLY-FIRST-ORDER PHASE TRANSITION. EFFECT OF UNIAXIAL PRESSURE ON THE ORIENTATIONAL ORDERING IN SOLID C_{70}

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The effect of external conjugated field on the weakly-discontinuous first-order phase transition is analyzed within Landau theory. The third-degree term in the Ginzburg–Landau expansion is shown to preserve the phase transition for some external fields in a contrast with the second-order case. The free energy expansion is shown to correspond to the second-order phase transition under the action of "effective" external field, that depends on both temperature and real field. The case of orientational phase transition in solid C_{70} is considered and the transition thermoelastic phenomena caused by the coupling of order parameter with elastic strain is analyzed. It is shown that the uniaxial mechanical pressure along the direction of 3-fold axis appears to be an external conjugated field for orientational ordering in crystalline C_{70}.

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It is well-known that the temperature-induced continuous (second-order) phase transition disappears under the action of arbitrary small external field conjugated to the order-parameter[1]. In the Landau theory of a weakly-discontinuous first-order phase transition[2, 3] an applied field conjugated to the order parameter shifts the transition temperature instead of suppressing the transition itself. In the present Letter I show that the weakly-discontinuous first-order phase transition is equivalent within Landau theory to a second-order one under the action of "effective" external field and the transition temperature corresponds to a zero value of this "effective" field.

The orientational ordering in a solid C_{70} is considered as an example and the external uniaxial pressure appears to play a role of conjugated field due to bilinear coupling of the phenomenological order parameter with symmetryzed homogeneous strain. The uniaxial pressure is shown to shift the transition temperature and change the temperature range of the co-existence of low- and high-temperature phases. The transition singularity in the shear modulus is shown to appear for some critical value of external pressure.

If the symmetry breaking associated with phase transition is known a priory then one can use the scalar order parameter corresponding to a unit representation of the symmetry group of low-symmetry phase [4] and the Ginzburg–Landau

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expansion for the weakly-first-order phase transition has a form [1, 2]

$$\Delta\mathcal{G} = \frac{a}{2}(T - T_c)\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 - E\eta \ , \tag{1}$$

where E is an external field conjugated to the phenomenological order parameter η and the system symmetry admits non-zero third-degree coefficient B, which we suppose being negative for convenience. Dimensionless expression

$$\Delta\tilde{\mathcal{G}} = \frac{C^3}{B^4}\Delta\mathcal{G} = \frac{\tau}{2}\,\zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4} - \sigma\zeta \ , \tag{2}$$

with

$$\tau = \frac{aC(T-T_c)}{B^2}, \quad \eta = -(B/C)\zeta \quad \text{and} \quad \sigma = -\frac{C^2}{B^3}E$$

describes a first-order transition which in the absence of external field ($\sigma = 0$) has a temperature $\tau_* = 2/9$ and corresponds to a finite jump of the order parameter $\Delta\zeta = 2/3$. The temperature range of the possible co-existence of a high-temperature phase, where $\zeta = 0$, and a low-temperature one ($(\zeta = (1 + \sqrt{1 - 4\tau})/2)$ is confined by their limits of stability, $\tau = 0$ and $\tau = 1/4$, respectively.

Substituting $\zeta = \tilde{\zeta} + 1/3$ into the Ginzburg–Landau expansion (2), we get the third-degree term excluded

$$\Delta\tilde{\mathcal{G}} = \frac{\tilde{\tau}}{2}\ \tilde{\zeta}^2 + \frac{\tilde{\zeta}^4}{4} - \tilde{\sigma}\tilde{\zeta} \ , \tag{3}$$

where

$$\tilde{\tau} = \tau - \frac{1}{3} \quad \text{and} \quad \tilde{\sigma} = \sigma - \frac{\tau}{3} + \frac{2}{27}.$$

Eq.(3) can be considered as the Ginzburg–Landau expansion corresponding to the "effective" external field $\tilde{\sigma}$ applied to the system undergoing the second-order phase transition with the order parameter $\tilde{\zeta}$ under the change of "effective" temperature $\tilde{\tau}$. The transition takes place between the states, associated with different minima of the Gibbs free energy. Both of these minima have non-zero values of "real" order parameter η, because the symmetry is broken already by the applied field for any temperature. The minimization of the Gibbs free energy (3) with respect to $\tilde{\zeta}$ for $\sigma \neq 0$ leads to a cubic equation

$$\tilde{\zeta}^3 + \tilde{\tau}\tilde{\zeta} - \tilde{\sigma} = 0 \tag{4}$$

with discriminant

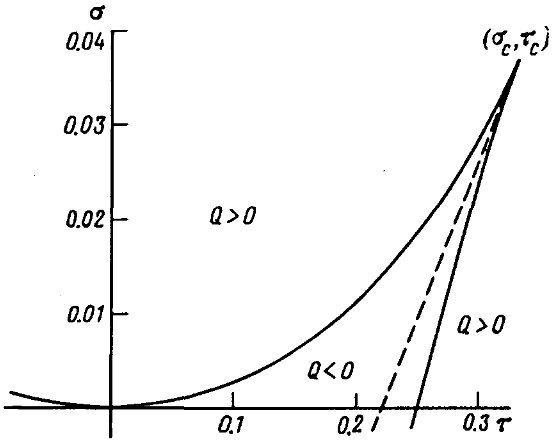
$$Q = \left(\frac{\tilde{\tau}}{3}\right)^3 + \left(\frac{\tilde{\sigma}}{2}\right)^2 \propto 4\sigma + 27\sigma^2 - 18\sigma\tau - \tau^2 + 4\tau^3 \ . \tag{5}$$

The cubic equation is known [5] to have one solution in real numbers for $Q > 0$ and three ones for $Q < 0$. Thus, the additional minimum of the Gibbs free energy corresponding to the co-existence of two phases appears for $\sigma_1 \leq \sigma \leq \sigma_2$ with

$$\sigma_{1,2} = -\frac{2}{27}\left(1 \pm (1 - 3\,\tau)^{3/2}\right) + \frac{\tau}{3} \ , \tag{6}$$

leading to the transition hysteresis in an external field

$$\Delta\sigma = \frac{1}{27}(4\,(1 - 3\,\tau)^{3/2}) \ .$$



The region of the phase coexistence. The dashed line corresponds to points of the first-order phase transition. It terminates in the critical point ($\tau_c = 1/3, \sigma_c = 1/27$)

The (τ, σ) phase diagram is shown at the Figure.

It might be proven rigorously that two different minima of the $\Delta\tilde{\mathcal{G}}(\tilde{\zeta})$ curve have different energies throughout all the temperature region of the phase coexistence. Only in the case of $\tilde{\sigma} = 0$ the phases have equal energies because of the degeneracy with respect to sign of $\tilde{\zeta}$. This determines the effect of applied field on the transition temperature τ_*

$$\tau_*(\sigma) = 3\sigma + 2/9 \ . \tag{7}$$

For $\sigma = 0$ we get naturally $\tau_*(0) = 2/9$. As the line of first-order transition in the (τ, σ) phase diagram separates states without the symmetry-breaking relation [1], it terminates in a (tri-)critical point ($\tau_c = 1/3$, $\sigma_c = 1/27$). The jump in the order parameter between the free energy minima

$$\Delta\zeta = \frac{2}{3}\sqrt{1 - 27\sigma}$$

vanishes at the critical point, hence, the weakly-first-order phase transition disappears for $\sigma > \sigma_c$. In a contrast with the second-order case where arbitrary small external field destroys the phase transition, here we find that the transition is preserved in the fields lower than σ_c.

Let us consider the thermoelastic phenomena around an orientational ordering transition in crystalline C_{70} [6–8]. The molecules of C_{70} are elongated in the direction of five-fold symmetry axis and have D_{5h} symmetry. The high-symmetry state of solid C_{70} is the FCC lattice with free rotation of molecules around the lattice nodes. In some cases the HCP lattice has been found in a high-temperature phase. The first ordering transition taking place at the temperature around 340 K freezes the molecular rotations into the revolution around long axis with orientation of these axes in $\langle 111 \rangle$ directions of FCC lattice or along c axis in HCP lattice. The lattice point symmetry decreases at the transition to rhombohedral (D_{3h}) and relevant representation of the space group has zero q. Second phase transition at lower temperature freezes the rotation around long axis and reduces symmetry further to monoclinic space group. We will consider the first transition for the case of FCC lattice in high-temperature phase. The HCP lattice can be treated in a similar way after the reorientation of coordinate axes.

The order parameter for this transition is traceless tensor of the second rank $\hat{\eta}$ [9]. Its independent components form 5D representation of cubic point group that contains its 2D and 3D irreps. The 3D one composed by non-diagonal elements appears to be relevant for the transition because it includes unit representation of the D_{3h} point symmetry group of low-symmetry phase. Corresponding invariant linear combination has a form $\eta_{xy}+\eta_{yz}+\eta_{xz}$, thus, we get $\eta_{xy}=\eta_{yz}=\eta_{xz}=\eta$ in a low-temperature state and the single component Ginzburg–Landau expansion (2) can be used. There is no external field directly conjugated to the orientational order parameter, however, the order parameter has the same transformational properties as does the strain tensor, hence, bilinear coupling with elastic strain is possible. Resulting Ginzburg–Landau expansion has a form

$$\Delta \mathcal{G}(T,P,\eta)=\frac{a}{2}(T-T_c)\eta^2+\frac{B}{3}\eta^3+\frac{C}{4}\eta^4+\Delta \mathcal{G}_{0,3}+\Delta \mathcal{G}_{int}, \tag{8a}$$

with pure elastic [10] and coupling energies, respectively,

$$\Delta \mathcal{G}_{0,3}=-\alpha_v K_0(T-T_c)\,\epsilon_0+\frac{K_0}{2}\epsilon_0^2+P\epsilon_0+\frac{K_3}{2}\epsilon_3^2+E_3\epsilon_3 \ , \tag{8b}$$

$$\Delta \mathcal{G}_{int}=D_3\,\eta\,\epsilon_3+D_0\,\eta^2\epsilon_0 \ , \tag{8c}$$

where α_v is a volume thermal expansion coefficient, K_0 is a bulk modulus and $K_3=C_{44}$ is shear modulus for the high-symmetry phase. The elastic energy includes not only effect of hydrostatic pressure P but also a uniaxial one E_3 along $\langle 111\rangle$ direction which coincides with the symmetry breaking [11]. Eqs.(8b) and (8c) use the symmetryzed cubic strains [12]:

$$\epsilon_0=\frac{1}{\sqrt{3}}(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}) \ , \tag{9a}$$

$$\epsilon_1=\frac{1}{\sqrt{6}}(-\epsilon_{xx}-\epsilon_{yy}+2\epsilon_{zz}) \ , \tag{9b}$$

$$\epsilon_2=\frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy}) \ , \tag{9c}$$

$$\epsilon_3=\sqrt{2}\epsilon_{yz} \ , \qquad \epsilon_4=\sqrt{2}\epsilon_{xz} \ , \qquad \epsilon_5=\sqrt{2}\epsilon_{xy} \ . \tag{9d}$$

Minimization of (8) with respect to strain gives

$$\epsilon_0(T,P,\eta)=\alpha_v\,(T-T_c)-\frac{P}{K_0}-\frac{D_0}{K_0}\eta^2 \ , \tag{10}$$

$$\epsilon_3(T,P,\eta)=-\frac{E_3}{K_3}-\frac{D_3}{K_3}\eta \ . \tag{11}$$

Eqs.(10) and (11) imply the lattice expansion in the $\langle 111\rangle$ direction due to molecular ordering

$$\frac{\Delta L_{\langle 111\rangle}}{L_{\langle 111\rangle}}=\frac{\epsilon_0}{\sqrt{3}}+\sqrt{2}\epsilon_3=-\frac{1}{\sqrt{3}}\frac{D_0}{K_0}\,\Delta\eta^2-\sqrt{2}\frac{D_3}{K_3}\,\Delta\eta \ , \tag{12}$$

which has been found around 6% in dilatometry and X-ray experiments [13]. Substituting (10) and (11) into Gibbs free energy (8) we get renormed Ginzburg–Landau expansion:

$$\Delta \mathcal{G}(T,P,E_3,\eta)=\Delta \mathcal{G}_{0,3}+\frac{a'}{2}\,(T-T_c')\,\eta^2+\frac{B}{3}\,\eta^3+\frac{C'}{4}\,\eta^4-E'\eta \ , \tag{13}$$

with the coefficients

$$a' = a + 2\alpha_v D_0 \ , \tag{14a}$$

$$T_c' = T_c + \frac{D_3^2}{2a'K_3} + \frac{2D_0}{K_0 a'} P \ , \tag{14b}$$

$$C' = C - \frac{2D_0^2}{K_0} \ , \tag{14c}$$

$$E' = \frac{D_3 E_3}{K_3^2} \ . \tag{14d}$$

Here $\Delta\mathcal{G}_{0,3}(T,P)$ is an elastic expansion energy of a high-symmetry phase with $\eta = 0$.

Thus, hydrostatic pressure shifts the transition temperature T_c (14b), whereas uniaxial pressure E_3 plays a role of external field conjugated to order parameter. From (7) and (14b) we can find an equation for a line of the first-order transition on the (T, P, E_3) phase diagram:

$$T_*' = T_c + \frac{D_3^2}{2a'K_3} + \frac{2B^2}{9a'C'} + \frac{2D_0}{K_0 a'} P - \frac{3C'}{a'B} \frac{D_3}{K_3^2} E_3 \tag{15}$$

with the critical values of temperature and uniaxial pressure given by the expressions

$$T_{cp}' = T_c' + \frac{B^2}{3a'C'} \quad \text{and} \quad E_3^{(cp)} = -\frac{B^3 K_3^2}{27 D_3 C'^2} \ . \tag{16}$$

The critical hydrostatic pressure depends linearly on the temperature

$$P_{cp}(T) = \frac{K_0}{2D_0}\left(a'(T - T_c') - \frac{B^2}{3C'}\right) \tag{17}$$

and vanishes when T goes to T_{cp}'.

The coupling (8c) of the order parameter with shear strain leads to the increase of shear stiffness caused by the additional degrees of freedom associated with molecular ordering

$$\left(\frac{1}{K_3}\right)_{tr} = -\frac{\partial^2}{\partial E_3^2}\left(\Delta\mathcal{G}(T,P,E_3,\eta) - \Delta\mathcal{G}_{0,3}\right) = \frac{D_3^2}{K_3^4}\left(\frac{\partial^2 \Delta\mathcal{G}}{\partial \eta^2}\right)^{-1} \ . \tag{18}$$

Using the technique described in Sec.*IV.E.2* of Ref.[11] for calculation of the thermal expansion and compressibility singularities around the weakly first-order ferroelastic transition under the action of conjugated field one can obtain the value of contribution to shear stiffness at the transition temperature $T = T_*'$:

$$\left(\frac{1}{K_3}\right)_{tr} = \frac{9}{2}\frac{C' D_3^2}{B^2 K_3^4}\left(1 - \frac{E_3}{E_3^{(cp)}}\right)^{-1} \ . \tag{19}$$

This contribution is the same for both high- and low-temperature phases. For the continuous transition (case of $B = 0$) shear stiffness diverges at the transition temperature corresponding to the singularity in susceptibility [2]. Divergence appears also near the critical point of the first-order transition $E_3^{(cp)}$.

The experimental data currently available do not allow us to determine the coefficients in the Ginzburg–Landau expansion (14) and to test our model quantitatively, however, qualitative implications appear to agree with the results of experimental studies. Linear shift of the transition temperature by applied pressure was found in various experiments [14, 15] with $dT_*/dP \approx$ 300 K/GPa and $dT_*/dE_3 \approx$ -1000 K/GPa and $\approx$ -1700 K/GPa on cooling and heating, respectively. The uniaxial pressure appears [15] to reduce the temperature hysteresis of the transition, which is in agreement with the phase diagram shown in the Figure, where the external field reduces the width of temperature interval of the co-existence of low- and high-symmetry phases narrower. The single crystals of C_{70} are very brittle and even small values of external force combined with large transition strain destroy the experimental specimens, so even remote vicinity of the critical point can not be reached. However, considerable anomaly in the shear elastic constant C_{44} has been observed [15].

To conclude, we have analyzed the effect of external conjugated field on the weekly-discontinuous phase transition within Landau theory. The external field leads to linear shift of the transition temperature and reduces the width of a region of possible co-existence of low- and high-symmetry phases. The transition line on a phase diagram terminates in a critical point. In a contrast with continuous transition where arbitrary small external field suppresses the transition the first-order transition disappears only in a supercritical fields. The orientational ordering transition in a crystalline C_{70} is shown to be an unusual implementation this model due to bilinear coupling of the phenomenological order parameter with lattice strain that makes a uniaxial pressure along three-fold symmetry axis play a role of conjugated external field. The linear shift of the transition temperature by external hydrostatic as well as uniaxial pressure appearing in the present model is in a qualitative agreement with the results of experimental studies along with decrease in the transition hysteresis under uniaxial pressure and a transition anomaly in a shear stiffness.

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